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Effect of substituted alkyl groups on textural properties of ORMOSILs

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A series of organically modified silica gels (ORMOSILs) with different alkyl groups such as methyl, ethyl, propyl, phenyl and octyl groups was investigated to determine the effect of substituted alkyl groups on the textural properties such as surface area, total pore volume, microporosity and hydrophobicity. Gelation time increased with increasing volume of alkyl groups. As-synthesized xerogels showed a systematic decrease in surface areas and total pore volumes and increase in microporosities with an increase in the volume of alkyl groups. All the ORMOSILs exhibited similar surface areas and total pore volumes after calcination at 500 °C for 1 d. Increase in microporosities was observed in all the calcined xerogels. This study suggests that the primary particle sizes of pure silica cores are not affected by the size of the alkyl group, while their connectivity decreases with increasing volume of alkyl groups in the acid–base catalysed system of alkyltrimethoxysilane–tetramethylorthosilicate. *© 1998 Kluwer Academic Publishers*

1. Introduction

Composite organic–inorganic materials have attracted a great deal of interest for achieving novel properties which are unattainable by the separate precursors. Organically modified silica gels (ORMASILs), are the representative family of organic–inorganic materials. They have been used for adsorption of metal ions from non-aqueous solutions, pre-concentration and separation of metallic ions [1–3]. They have many other potential applications in the development of ceramic precursors, solid-state tunable lasers, softer abrasives, adhesives, ion exchangers, and carriers for enzymes and cells [1, 4, 5].

ORMOSILs can be prepared by two different ways: (a) coating (grafting) silica gels by an organic-substituted silicon alkoxide (T precursors such as methyl or ethyltriethoxysilane) [1, 2], and (b) synthesizing from a mixture of a tetraalkoxysilane like tetraethoxy- or tetramethoxysilane and an organic-substituted silicon alkoxide by the sol–gel method [6–9]. In the former case (the coating method), the modification of textural properties depends mainly on the interaction between the surface of the original silica gel and the modifying agent, whereas in the latter case (the sol–gel method), a number of gel properties are influenced and furthermore gels can be tailored by manipulating many factors such as preparation parameters and physicochemcial properties of the modifying agent.

Recently, studies on the kinetics of the involved reactions such as relative hydrolysis rates of each component and self- and cross-condensation reactions and on application of ORMOSILs are being widely conducted, using the sol–gel method to achieve the desired properties with high purity and homogeneity [8–19]. However, the focus on the textural properties of ORMOSIL xerogels was limited and the results were inconsistent [6, 15–17]. Witte *et al.* [6] observed that the introduction of organic groups into the gel network led to a decrease of the surface area, pore volume and pore-size distribution in the acid–base catalysed system of tetramethylorthosilane–methyltrimethoxysilicate. Schwertfger *et al.* reported [15] that the increase of T precursor content up to 20 mol% caused an increase in surface area and a decrease in density in the base-catalysed system of tetramethylorthosilane–methyltrimethoxysilicate, while Fahrenholtz and Smith [16] found a decrease of surface area with increase of dimethyldiethoxysilane in the base-catalysed system of tetraethylorthosilicate–dimethyldiethoxysilane.

The substituted organic groups of the precursors greatly influence the textural properties such as surface area, microporosity, pore volume and pore-size distribution, as well as the surface functionality and hydrophobicity [6, 15, 16, 18, 19]. The controlled textural properties are important and sometimes essential to the ORMOSIL applications. The tailoring of these properties has been attempted previously by using a specific precursor as functional group and/ or structure-directing template, and by changing its

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content in the framework [1, 6, 13, 18–20]. However, very limited information is available for evaluating the exact effect of organic group on the textural properties such as surface area, porosity and pore volume. Therefore, a better understanding of the effect of organic group on the textural properties is necessary to the exploitation of these ORMOSILs for various applications. This paper deals with the characterization of a series of ORMOSILs with different alkyl groups in order to investigate the effect of substituted alkyl groups on the textural properties such as surface area, total pore volume, microporosity and hydrophobicity.

2. Experimental procedure

2.1. Synthesis of ORMOSILs

Five ORMOSILs were synthesized through the acid–base catalysed two-step route by sol–gel method. Tetramethylorthosilicate (TMOS) diluted with ethanol was mixed with methyltriethoxysilane (MeTEOS), ethyltrimethylsilane (EtTMOS) propyltrimethylsilane (PrTMOS) or phenyltrimethylsilane (PhTMOS) typically at the molar ratios of 3 TMOS: 1 T precursors. Octyltriethoxysilane (OcTEOS) was mixed at the ratio of 1/6 with TMOS because a higher ratio resulted in two separate phases on addition of acidified water (even after 2 d). Acidified water was slowly added to these solutions to hydrolyse silicon alkoxides. The molar composition of the initial sol was 1 alkoxide : 5 ethanol : 1.5×10^{-3} HCl : 3.75 H_2O. After the initial sols were completely cooled at room temperature for at least 6 h, their pHs were adjusted to the value of 8.2 ($\pm$ 0.1) using 0.5 N NH_4OH solution. The gels were kept at room temperature in capped plastic bottles for 48 h after gelation. The resultant gels were dried at 70 °C for 2 d and at 150 °C for at least 12 h in an oven. Part of each dried ORMOSIL was calcined at 500 °C (heating rate = 4 °C min^{-1}) for 24 h to remove organic materials. All the xerogels were kept in capped vials for characterization.

2.2. Nitrogen adsorption/desorption and water adsorption isotherms

Nitrogen adsorption/desorption isotherms were obtained using Quantachrome Autosorb-1 at liquid nitrogen temperature after degassing at 150 °C under 0.01 torr (1 torr = 133.322 Pa). Surface area was estimated using the multi-point BET fit. Micropore volume was estimated by the *t*-method. The total pore volume was obtained using the adsorption data of the nitrogen isotherm at relative pressure of 0.99. Microporosity was expressed as the percentage of micropore volume in total pore volume. Water adsorption isotherms were measured after degassing samples at 150 °C, is described elsewhere [18, 19].

3. Results and discussion

3.1. Gelation time

Gelation is well known to take place through hydrolysis and polymerization reactions. With regard to monoorganic-substituted T precursors, gelation was greatly affected by the steric bulk and electron characteristics (alkyl groups exhibit electron-providing property) [14, 17]. Fig. 1 shows the effect of alkyl group on the gelation time.

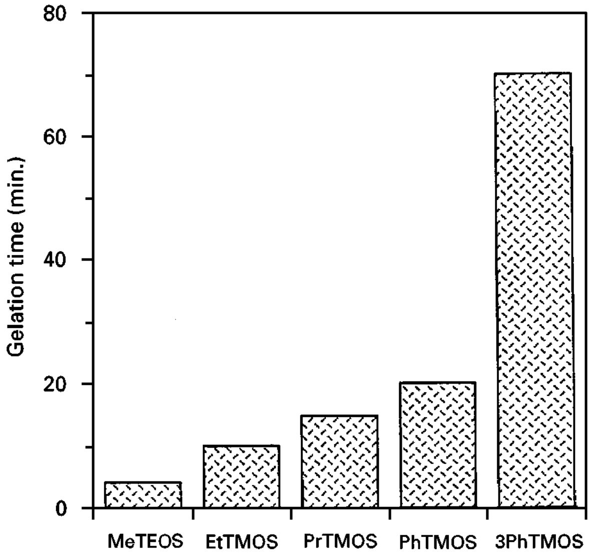

Figure 1 Effect of alkyl group on gelation time.

Gelation time increased with the carbon chain length attached to the silicon atom or the content of T precursor. While MeETOS sol gelled within 4 min (MTOS sol gelled immediately) after the adjustment of pH to 8.2 with NH_4OH solution, the gelation time of 3PhTMOS sol was 70 h. The hydrolysis rate of T precursor increased with increase in the length or branching (volume) of alkyl groups under acidic conditions (inductive effect) [14, 17]. On the other hand, the steric effect predominated the polymerization reaction above a certain level of T precursor content to result in a longer gelation time with increasing volume of alkyl groups [17]. In addition to the steric effect, the lower functionality of T precursors retarded gelation because of the reduced cross-linking reaction [7, 16]. Because only monoalkyl-substituted T precursors with different volumes and acid-base two step procedure were employed in this study, the functionality and the hydrolysis rate did not affect gelation much in all cases. Therefore, it seems that gelation was mainly affected by the steric effect in this study.

3.2. Hydrophobicity of synthesized ORMOSILs

The hydrophobicity of synthesized ORMOSILs was examined by the water adsorption isotherms. The water adsorption isotherms showed different hydrophobicities depending upon alkyl group and its content, as shown in Fig. 2.

All the as-synthesized xerogels exhibited a moderate type III isotherm indicating hydrophobicity. With increasing volume of alkyl group in T precursors, the amount of adsorbed water decreased. The amount of adsorbed water was highest in MeTEOS xerogel and lowest in 3PhTMOS xerogel over the complete range of relative pressures (adsorption data below the

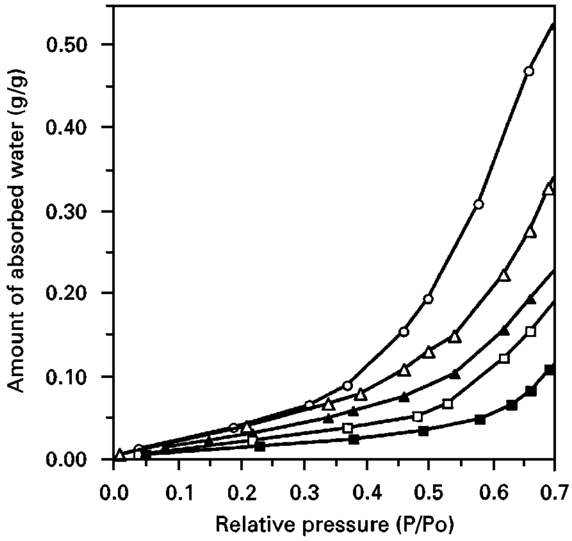

Figure 2 Water adsorption isotherms of as-synthesized ORMOSILs: (○) MeTEOS, (△) EtTMOS, (▲) PrTMOS, (□) PhTMOS, (■) 3PhTMOS.

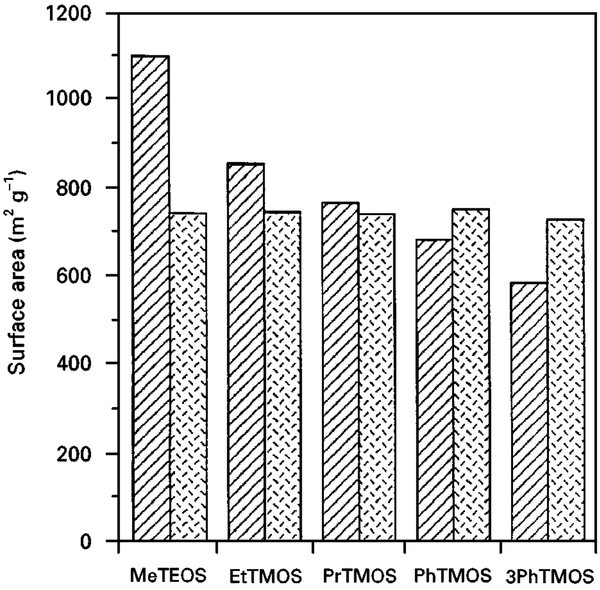

Figure 3 Effect of alkyl group on surface areas of xerogels before and after calcination. ▨ As-synthesized, ▦ Calcinated.

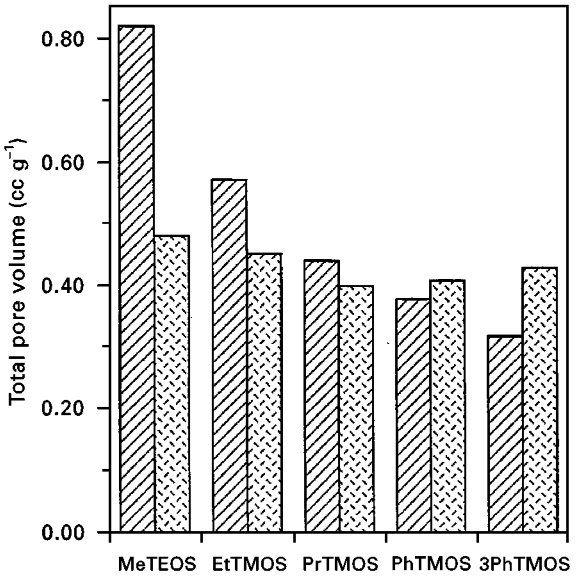

Figure 4 Effect of alkyl group on total pore volumes of xerogels before and after calcination. ▨ As-synthesized, ▦ Calcinated.

relative pressure of 0.7 are only shown in Fig. 2 for clear comparison). It appears that hydrophobicity is linearly proportional to the hydrophobic properties of the organic groups in T precursors. This result implies that the organic groups may have been distributed similarly in all the as-synthesized xerogels, i.e. mainly on the gel surface.

3.3. Gel texture

Gel textures of the as-synthesized and calcined ORMOSILs were examined to evaluate the effect of alkyl groups on the gel texture. The calcination temperature of 500 °C was chosen in this study, based on the published results that organic groups like methyl, dimethyl or propylmethacryl group were destroyed below this temperature [6, 19, 20].

All xerogels including the calcined xerogels, except for the as-synthesized MeTEOS and TMOS xerogels, showed type I nitrogen isotherm. The as-synthesized MeTEOS exhibited type IV isotherm with hysteresis, whereas the calcined MeTEOS xerogel showed type I isotherm. The gel textures of both as-synthesized and calcined xerogels are shown in Figs 3–5. The textural properties of TMOS and OcTEOS xerogels are also summarized in Table I for comparison.

Consistent decreases in surface area and total pore volume were observed in the as-synthesized xerogels as the volume of alkyl groups increased. Surface areas of as-synthesized xerogels decreased from 1100 m^2 g^{-1} for MeTEOS xerogel to 568 m^2 g^{-1} for 3PhTMOS xerogel. Similarly, total pore volumes decreased from 0.82 cm^3 g^{-1} for MeTEOS xerogel to 0.32 cm^3 g^{-1} for 3PhTMOS xerogel. However, no consistent relationship in the surface area and total pore volume was found among the calcined xerogels. Calcination resulted in a decrease of surface areas and total pore volumes in MeTEOS, EtMTOS and PrTMOS xerogels, while they increased in 25PhTMOS, 33PhTMOS and OcTEOS xerogels after the calcination. The removal of organic groups from xerogels resulted in similar surface areas and total pore volumes regardless of the alkyl group in T precursors. Their variation among the calcined xerogels were less than 10% (total pore volume of MeTMOS and OcTEOS were not within this error range). Moreover, comparing the surface areas of the as-synthesized xerogels in terms of unit volume, all xerogels except for 3PhTMOS (760 m^2 cm^{-3}) and OcTEOS (709 m^2 cm^{-3}) xerogels showed similar surface areas in the range of 820–860 m^2 cm^{-3}. On the other hand, a continuous increase in microporosity was observed with increasing volume of alkyl groups in both the as-synthesized and calcined xerogels. The calcination resulted in a significant increase in microporosity for all the xerogels. The microporosity increased from 31% to 58% in MeTEOS xerogel and from 50% to 79% in

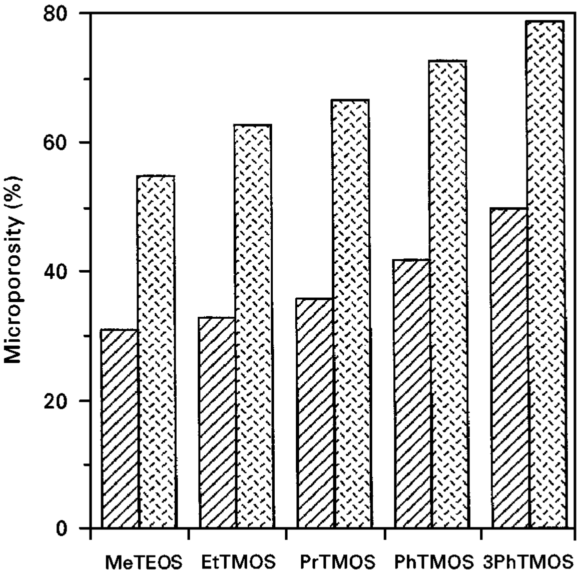

Figure 5 Effect of alkyl group on microporosities of xerogels before and after calcination. ▨ As-synthesized, ▩ Calcinated.

3PhTMOS after calcination. Relatively high deviation of 3PhTMOS and OcTEOS xerogels from the other xerogels seemed to result from the different composition of initial sol.

A two-step procedure in ORMOSIL preparation results in xerogels composed of pure silica cores with organic groups mainly on their surface, as has been shown earlier [6, 16, 19]. The presence of substituted organic groups results in the reduction of network connectivity and of surface tension [6, 7, 16, 17]. The reduced connectivity leads to a less stable and more flexible network which easily undergoes strong contraction, whereas low surface tension prevents the collapse of the gel structure. Both effects cause an increase in microporosity. At low organic content (less than approximately 30% of MeTMOS/TMOS system), the latter effect predominates to result in the increase of surface area and pore volume [15, 16]. However, as the volume of alkyl group increases, the network connectivity is reduced due to the steric effect. When the latter effect counteracts the former effect, surface area and pore volume decrease [16, 17]. A similar result was also observed in this study. When MeTEOS xerogel was compared to TMOS xerogel, MeTEOS xerogel showed higher surface area ($1100\,m^2\,g^{-1}$) and total pore volume ($0.82\,cm^3\,g^{-1}$) than those of TMOS xerogel (Table I). On the other hand, the decrease in surface area and total pore volume with bulky alkyl group suggests that the steric effect seems to be dominant in determining the gel structure in this study, as also indicated in the gelation times (Fig. 1).

The network connectivity decreased with the bulky size of the organic groups to result in the decrease of surface area and pore volume and in the increase of microporosity. The high network connectivity was also indicated in the type IV nitrogen isotherm of TMOS and MeTEOS xerogel and in relatively high total pore volume ($0.48\,cm^3\,g^{-1}$) of the calcined MeTEOS xerogel. However, primary particles of pure silica cores seems to consist of similar sizes in all the as-synthesized xerogels, because the surface areas of the as-synthesized xerogels were similar on a volume basis, and furthermore, these xerogels also showed similar surface areas and pore volumes after calcination. The increase or decrease of surface area and pore volume depending on the organic group could be explained by the similar particle sizes of pure silica cores. Calcination caused the removal of organic groups and the dehydroxylation of surface hydroxyl groups without a significant change in the primary particle size of pure silica. Because the particle sizes of pure silica cores were similar and the organic groups were located mainly at the gel surface in all the as-synthesized samples, the resultant xerogels showed similar surface areas and pore volumes. However, the network connectivity decreased with bulky organic groups, which led to the formation of micropores. Therefore, the consistent increase in microporosity with the bulky size of organic groups even after calcination seems mainly due to the reduced network connectivity. Another reason seems to be that the alkyl groups prevented the collapse of micropores during calcination, as Yamane *et al.* suggested [21]. Otherwise, micropores are destroyed in the temperature range of 400–500 °C [17, 21]. The presence of alkyl groups also seemed to contribute to the significant increase of microporosity after calcination.

4. Conclusion

A two-step procedure in ORMOSIL preparation led to xerogels composed of pure silica cores with organic groups mainly on their surface. In the acid–base catalysed system of alkyltrimethoxysilane–tetramethylorthosilicate, the sizes of primary particles were not affected by the volumes of alkyl groups, while network connectivity decreased with sizes of alkyl groups to result in a decrease of surface area and total pore volume, and an increase of microporosity.

TABLE I Textural properties of TMOS and OcTEOS xerogels

Xerogel	Gelation time (min)	Surface area ($m^2\,g^{-1}$)	Total pore volume ($cm^3\,g^{-1}$)	Microporosity (%)
As-synthesized TMOS	< 1	1000	0.81	29
OcTEOS				
as-synthesized	12	549	0.32	56
calcined		747	0.39	70

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